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THE DISCOVERY OF A NEW INFRARED EMISSION FEATURE AT 1905 WAVENUMBERS (5.25 MICRONS) IN THE SPECTRUM OF BD +30°3639 AND ITS RELATION TO THE POLYCYCLIC AROMATIC HYDROCARBON MODEL

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ABSTRACT

We have discovered a new IR emission feature at 1905 cm^{-1} (5.25 μm) in the spectrum of BD +30°3639. This feature joins the family of well-known IR emission features at 3040, 2940, 1750, 1610, "1310," 1160, and 890 cm^{-1} (3.3, 3.4, 5.7, 6.2, "7.7," 8.6, and 11.2 μm). The origin of this new feature is discussed and it is assigned to an overtone or combination band involving C—H bending modes of polycyclic aromatic hydrocarbons (PAHs). Laboratory work suggests that spectral studies of the 2000–1650 cm^{-1} (5.0–6.1 μm) region may be very useful in elucidating the molecular structure of interstellar PAHs. The new feature, in conjunction with other recently discovered spectral structure, suggests that the narrow IR emission features originate in PAH molecules rather than large carbon grains. Larger species are likely to be the source of the broad underlying "plateaus" seen in many of the spectra.

Subject headings: infrared: spectra — interstellar: grains — interstellar: molecules

I. INTRODUCTION

Many celestial objects show a distinctive set of emission features in the infrared, known collectively for many years as the unidentified infrared emission bands (UIR bands). The strongest fall at 3040, 2940, 1750, 1610, "1300," 1160 and 890 cm^{-1} (3.3, 3.4, 5.7, 6.2, "7.7," 8.6, and 11.2 μm) (Aitken 1981; Willner 1984). Objects which are known to produce these features include planetary nebulae (Russell, Soifer, and Willner 1977; Bregman *et al.* 1983; Cohen *et al.* 1986; and references therein), reflection nebulae (Sellgren, Werner, and Dinerstein 1983; Sellgren *et al.* 1985), H II regions (Russell, Soifer, and Merrill 1977), and galaxies (Aitken and Roche 1985). While the apperance of similar spectra in such a wide variety of objects suggests the band carriers are closely related, variations in the relative band intensities imply that they do not arise from a single carrier but from a family of related compounds (Cohen *et al.* 1986, 1989).

In 1981, Duley and Williams pointed out that a few of the bands fell at frequencies characteristic of polycyclic aromatic hydrocarbons (PAHs) and suggested that the bands were produced by aromatic units in thermally excited dust grains. This was extended by Leger and Puget (1984) and Allamandola, Tielens, and Barker (1985) who suggested that the features arise from free molecular PAHs rather than from dust grains (see Leger, d'Hendecourt, and Boccara 1987 and Allamandola and Tielens 1989 for reviews).

If PAHs are indeed responsible for the interstellar IR emission bands, weak features are predicted between 2000 and 1850 cm^{-1} (5.0–5.4 μm) since laboratory spectra of most PAHs contain weak bands in this region. Most published astronomical spectra in this region start at about 1920 cm^{-1} (5.2 μm) and extend to lower frequencies. The first few data points in these spectra hint that a new feature lies just at the edge of the range covered. To test the reality of this band, as well as to search for other spectral structure, the 2040–1470 cm^{-1} (4.9–6.8 μm) spectrum of BD +30°3639, a compact planetary nebula having bright infrared emission bands (e.g., Bently *et al.* 1984), was measured from the Kuiper Airborne Observatory.

II. OBSERVATIONS AND DATA

Spectra were obtained using the Faint Object Grating Spectrometer (FOGS), a liquid helium-cooled spectrometer employing an array of 24 Si:Bi detectors. The original system was described by Witteborn and Bregman (1984). It has since been modified to include an externally rotatable grating table and an aperture and order-sorting filter wheel. Data from 2040–1250 cm^{-1} (4.9–8.0 μm) were obtained from the Kuiper Airborne Observatory on 1987 September 1 and 3, using a 27″ focal plane aperture and a chopper throw of 2′. Spectral resolution was 0.044–0.37 μm per detector ($\lambda/\Delta\lambda = 130$–$210$). These spectra were obtained using four different grating settings with 10 beam switches and an integration time of 20 minutes at each setting. Spectra were also obtained from 1250–770 cm^{-1} (8.0–13.0 μm) from the NASA/Steward 60 inch (1.5 m) telescope on Mount Lemmon, Arizona on 1987 October 5 and 6. This system used a 12″ focal plane aperture and provided a spectral resolution of ~0.05 μm per detector ($\lambda/\Delta\lambda = 200$). A 1′ chopper throw was used. In both cases, the aperture encompassed the entire emission from the nebulae which is approximately 5″ in diameter. Wavelength calibration was performed by observing a blackbody source through either a polystyrene sheet or an ammonia gas cell, producing absorption bands at known wavelengths. Flux calibration and removal of telluric absorptions was achieved by observations of standard stars (α Her and β And from the KAO and α Tau from Mount Lemmon) with known photospheric temperatures.

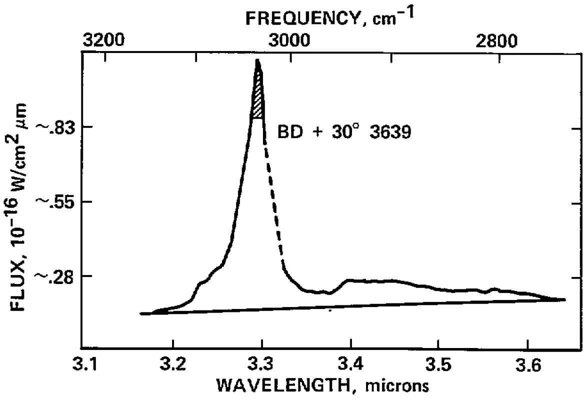

FIG. 1*a*

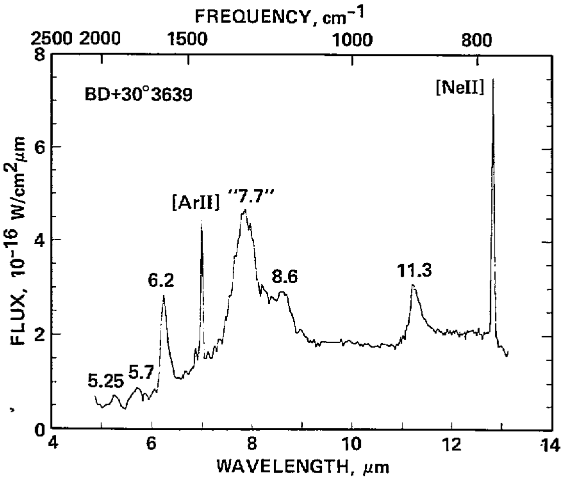

FIG. 1*b*

FIG. 1.—The 3170–770 cm^{-1} (3.15–13.0 µm) spectrum of BD +30°3639. (*a*) The 3170–2740 cm^{-1} (3.15–3.65 µm) spectrum is adapted from Geballe *et al.* (1984). (*b*) The 1000–770 cm^{-1} (10.0–13.0 µm) portion of spectrum (*b*) is adapted from Witteborn *et al.* (1989). The narrow bands due to atomic transitions of [Ar II] and [Ne II] are labeled. All other features are attributed to PAHs.

The 3170–2740 cm^{-1} (3.15–3.65 µm) and 2040–770 cm^{-1} (4.9–13.0 µm) spectra of BD +30°3639 are shown in Figures 1*a* and 1*b*. All the major IR emission bands attributed to PAHs are evident in this spectrum. The 2040–1470 cm^{-1} (4.9–6.8 µm) region is shown on an expanded scale in Figure 2. A new band at 1905 cm^{-1} (5.25 µm) is evident. Band positions and assignments are summarized in Table 1 (see Allamandola, Tielens, and Barker 1989).

III. NEW BAND ASSIGNMENT

The absorption spectra of several PAHs suspended in KBr pellets are shown in Figure 3 (Salisbury *et al.* 1988). All of these spectra have weak bands in the 2000–1800 cm^{-1} (5.0–5.6 µm) region. We assign these to combination or overtone bands involving C—H bending vibrations for the following reasons. The low intensity of the bands implies that they are due to a weakly allowed transition, a characteristic that is consistent with overtone and combination bands rather than fundamen-

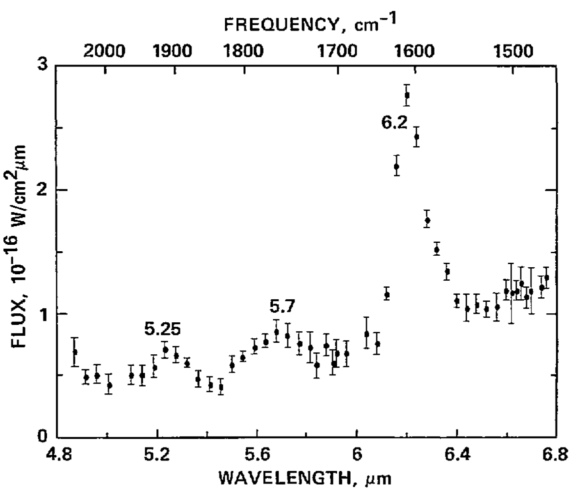

FIG. 2

TABLE 1

PAH BANDS IN BD +30°3639 AND ASSIGNMENTS

BAND POSITION λ (µm)	BAND POSITION ν (cm^{-1})	ASSIGNMENT
3.29	3040	C—H stretch
5.25	1905	Combination/overtone of C—H bends
5.7	1750	Combination/overtone of C—H bends, C=C stretch?, carbonyl C=O stretch?
6.2	1615	C=C stretch
"7.7"	"1300"	C=C stretch
8.7	1150	C—H in-plane bend
11.2	890	C—H out-of-plane bend

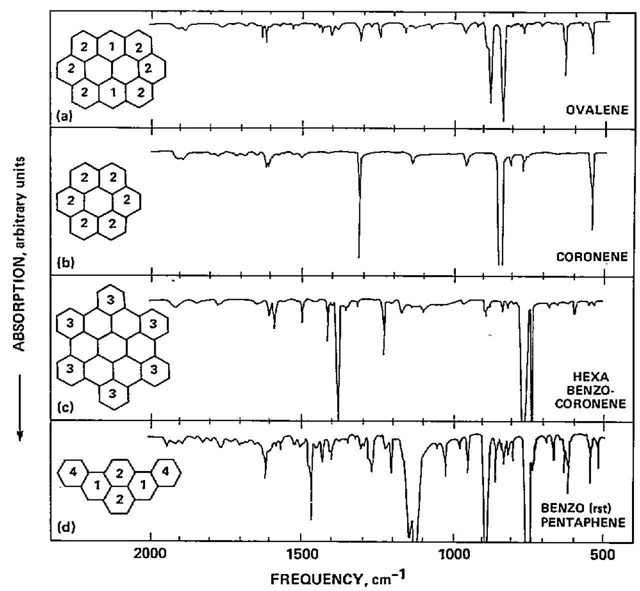

FIG. 3

FIG. 2.—The 2040–1470 cm^{-1} (4.9–6.8 µm) spectrum of BD +30°3639 showing the new 1905 cm^{-1} (5.25 µm) band as well as the previously known bands at 1750 and 1610 cm^{-1} (5.7 and 6.2 µm).

FIG. 3.—The absorption spectra of several PAHs suspended in KBr pellets. The numbers in the edge rings indicate the number of adjacent H atoms per ring. Note that all of these spectra have weak-to-moderate absorption features in the 2000–1800 cm^{-1} (5.0–5.6 µm) region. The spectra are adapted from Salisbury *et al.* (1988).

tals. This frequency domain falls between the 3100–2800 cm^{-1} (3.2–3.6 μm) C—H stretching and the 1650–1100 cm^{-1} (6.1–9.0 μm) C=C stretching ranges for PAHs. The only fundamentals which can combine to produce a band in this region are the C—H in-plane and out-of-plane bending vibrations which fall in the 1225–950 cm^{-1} (8.16–10.5 μm) and 900–650 cm^{-1} (11–15.4 μm) regions, respectively (Bellamy 1960). Overtone and combination bands often involve fundamental vibrations which are IR-forbidden or only weakly allowed and the presence of a weak band at about 1905 cm^{-1} (5.25 μm) does not require strong IR active bands at all the contributing fundamental frequencies in the bending regions (Herzberg 1968). Laboratory studies by S. Cyvin, P. Klaeboe, and coworkers (private communication) of the IR polarization behavior and Raman spectra of several PAHs support this assignment for bands falling near 1900 cm^{-1} (5.26 μm).

While bands in the 2000–1650 cm^{-1} (5.0–6.1 μm) region have not been discussed in the spectroscopic literature on the multiring PAHs, weak absorption band patterns in this region have long been used to identify substitution patterns on the single ring aromatic hydrocarbon benzene (Young, Duvall, and Wright 1951; see Bellamy 1960 for a review). Thus, we expect that the absorption features between 2000 and 1650 cm^{-1} (5.0 and 6.1 μm) can be used to probe ring substitution patterns. Inspection of the PAH spectra in Figure 3 shows that for PAHs with single, as well as doubly, or triply adjacent H atoms per edge ring, the overtone/combination band falls near 1905 cm^{-1} (5.25 μm), the position of the newly observed interstellar feature. In contrast, PAHs with more than three adjacent H atoms per edge ring produce bands closer to 2000 cm^{-1} (5.0 μm). The position of the new band implies molecular geometries consistent with those deduced on the basis of spectral structure in the 1000–700 cm^{-1} (10.0–14.3 μm) region (Cohen, Tielens, and Allamandola 1985; Witteborn *et al.* 1989) and the chemical stabilities of PAHs (Allamandola, Tielens, and Barker 1989). The overtone/combination bands in Figure 3 also show substructure which may be characteristic of the specific fundamentals responsible. This suggests that, once appropriate laboratory data become available, the 2000–1800 cm^{-1} (5.0–5.6 μm) region may provide important information about the edge structures of interstellar PAHs.

Due to PAH-PAH interactions, the intensities of C—H out-of-plane bending modes of PAHs suspended in KBr are greatly enhanced relative to all other vibrational modes (Allamandola and Sandford 1988). Such an enhancement is not found for free molecular PAHs. Thus, the low observed ratio of the interstellar features at 1905 and 890 cm^{-1} (5.25 and 11.2 μm) argues against an assignment of the narrow features to PAH units in carbon grains. Furthermore, the laboratory spectra of solid materials proposed to be responsible for the IR emission features such as hydrogenated amorphous carbon (HAC) films, quenched carbonaceous composite (QCC), and soot show no evidence for an absorption feature around 1905 cm^{-1} (5.25 μm) (Ogmen and Duley 1988; Sakata *et al.* 1987; Blanco, Bussoletti, and Colangeli 1988). Since pure molecular PAHs possess weak bands in this region, we see no reason to invoke other explanations to account for this feature.

IV. MOLECULAR PAHS AND THE IR EMISSION BANDS

Interstellar PAHs were first suggested to be responsible for the IR emission bands about 5 years ago. The recent detection of new features which also belong to this spectrum, including the 1905 cm^{-1} (5.25 μm) band, strengthen this model.

First, the wavelength of the C—H out-of-plane bending mode in PAHs is very sensitive to the edge structure of the molecule. The position of the 890 cm^{-1} (11.2 μm) band is indicative of PAHs having isolated H atoms on their edge rings. Since a family of PAHs is expected in the ISM, additional bands in the 1000–700 cm^{-1} (10.0–14.3 μm) region would be expected which correspond to molecules having two or more adjacent H atoms per edge ring. Detection of a plateau and additional weak features with varying relative intensities in this spectral region is completely consistent with the PAH model and indicates that the interstellar PAH population is dominated by structures having one, two, or three adjacent H atoms per edge ring (Cohen, Tielens, and Allamandola 1985; Roche, Aitken, and Smith 1989; Witteborn *et al.* 1989).

Second, because of the large anharmonicity of the C—H stretching mode, emission from upper vibrational levels should be displaced to longer wavelengths relative to emission from the C—H stretching fundamental (Barker, Allamandola, and Tielens 1987). Bands consistent with this anharmonicity are present at 2940 and 2840 cm^{-1} (3.4 and 3.52 μm) (Geballe *et al.* 1984, 1989; de Muizon *et al.* 1986). The anharmonicities associated with the C=C stretching mode responsible for the 1610 cm^{-1} (6.2 μm) feature and the C—H out-of-plane bending mode responsible for the 890 cm^{-1} (11.2 μm) feature are smaller and these bands should be skewed to the red (Barker, Allamandola, and Tielens 1987). Appropriate asymmetric profiles are a general characteristic of these two interstellar features (Bregman and Rank 1972; Bregman *et al.* 1983; Cohen *et al.* 1986; 1989; Witteborn *et al.* 1989; see also Fig. 1).

Third, in PAH spectra the majority of the bands in the 1400–1100 cm^{-1} (7.1–9.1 μm) region are due to C=C skeletal modes. The exact positions of these bands vary with the molecular structure of the PAH. If a family of PAHs is responsible for the IR emission it would be expected that the interstellar band near 1300 cm^{-1} (7.7 μm) would exhibit a variety of profiles dependent on the local PAH population. Such spectral variations have, in fact, been observed. The peak position of the "1300" cm^{-1} ("7.7" μm) feature has been found to range from 1320 to 1270 cm^{-1} (7.6 to 7.9 μm) (Bregman 1989; Cohen *et al.* 1989). Again, the findings are consistent with the PAH interpretation.

Finally, if PAHs are present in the ISM, the IR emission spectra should exhibit weak features due to combination and overtone bands of the fundamental vibrations of the PAHs. These include bands in the 2000–1650 cm^{-1} (5.0–6.1 μm) region. The discovery of the new band at 1905 cm^{-1} (5.25 μm) reported here represents yet another observation consistent with the PAH model.

V. CONCLUSION

The PAH hypothesis predicts the presence of a weak emission feature (or features) in the 2000–1650 cm^{-1} (5.0–6.1 μm) region in the spectra of objects which show the interstellar IR emission bands attributed to PAHs. The 2040–1250 cm^{-1} (4.9–8.0 μm) spectrum of BD +30°3639, a low-excitation, compact, planetary nebula known to emit the infrared features, was measured to search for such a band. A band at about 1905 cm^{-1} (5.25 μm) was indeed discovered, providing strong support for the PAH model. This new band is assigned to an overtone or combination band involving C—H in-plane and out-of-plane bending vibrations. Its presence and position support the picture that the interstellar PAH population is dominated by members containing edge rings with nonadjacent, as well as doubly and triply adjacent, H atoms.

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